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## THERMODYNAMIC POTENTIALS AND PROPERTIES

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### **THERMODYNAMIC POTENTIALS AND PROPERTIES**

We deal here with two thermodynamic subjects that in most other presentations are separately covered: 'Properties of pure substances', usually covered at the very beginning of Thermodynamic courses, and Potentials or 'General relations', usually covered at the very end of Thermodynamic courses. In our view, it is better to deal at the same time with the functional structure of Thermodynamic (which functions are needed and how others relate to them) and the actual models and particular values for those functions (the material properties of selected substances). If not, one might end without realising the minimum set of properties which define the thermodynamic behaviour of a substance, or the many important relations amongst them, as the relation between vaporisation enthalpy and vapour pressure data, the relation between the speed of sound and density data, etc.

It may be argued that the combined presentation of Potentials and Properties is too wide, but one may do a short combined presentation (even shorter than here done) and leave most details for discussion under other headings to follow: Phase changes, Real gases, Mixtures, etc.

Briefly, the aim here is to place on a common field the two isolated models of perfect gases and perfect liquids that we have freely used, showing how one can model any possible behaviours of a substance at any state, primarily for pure substances, but opening the door to any kind of mixture.

## TERMODYNAMIC POTENTIALS. SYSTEM EQUILIBRIUM

An isolated system is at equilibrium when its entropy is a maximum, but what about a non-isolated system?

We have introduced many state variables, like  $E$  (or  $U$ ),  $V$ ,  $S$ ,  $T$ ,  $p$ ,  $\mu_i$ , and  $\Phi$ , others being not state variables but path integrals, like  $W$ ,  $Q$ ,  $E_{\text{mdf}}$ ,  $S_{\text{gen}}$  and  $I$ . These state variables (many of them only defined at equilibrium states), and many others we intend to introduce to ease our thermodynamic analysis, are not all independent. In fact, the number of intensive independent variables at equilibrium, what is known as the variance of the system, is just 2 for simple compressible systems (without change in composition), and  $2+C-1$  for a single-phase multicomponent system with  $C$  different chemical species, as deduced in Chapter 2: Entropy, where we got  $T$ ,  $p$  and  $\mu_i$ ,  $(1+1+C)$  as intensive variables defining the equilibrium, and we got the Gibbs-Duhem equation as their only constraint.

Thermodynamic potentials are single functions of some variables (call them their eigenvariables) from which all other equilibrium variables can be deduced. The genuine thermodynamic potential is entropy, from which  $T$ ,  $p$  and  $\mu_i$  were derived in (2.4-5). We call eigenvariables the variables that were kept constant during the evolution towards equilibrium; in the case of entropy they were,  $U$ ,  $V$  and  $n_i$ , thus, the genuine thermodynamic potential is  $S(U, V, n_i)$ , and its total differential form  $dS=(1/T)dU+(p/T)dV-\sum(\mu_i/T)dn_i$ . From the many thermodynamic potentials one may define, we only consider the four energetic potentials:

$$\text{Internal energy: } U(S, V, n_i), dU=TdS-pdV+\sum\mu_i dn_i \quad (4.1)$$

$$\text{Enthalpy: } H(S, p, n_i) \equiv U+pV, dH=TdS+Vdp+\sum\mu_i dn_i \quad (4.2)$$

$$\text{Helmholtz function: } A(T, V, n_i) \equiv U-TS, dA=-SdT-pdV+\sum\mu_i dn_i \quad (4.3)$$

$$\text{Gibbs function: } G(T, p, n_i) \equiv U+pV-TS=H-TS=\sum\mu_i n_i, dG=-SdT+Vdp+\sum\mu_i dn_i \quad (4.4)$$

where Euler equation (2.13) has been used in (4.4). Any of the above thermodynamic potentials, as a function of its eigenvariables, contain all the thermodynamic information of the equilibrium states, and may be physically interpreted in a similar manner as entropy: entropy was a function that got extremal (maximum) as a system with constant  $U$ ,  $V$  and  $n_i$  (the eigenvariables) evolved towards equilibrium; similarly, internal energy is a function that gets extremal (minimum in this case, Fig. 4.1) as a system with constant  $S$ ,  $V$  and  $n_i$  (its eigenvariables) evolved towards equilibrium; similarly, enthalpy is a function that gets extremal (minimum) as a system with constant  $S$ ,  $p$  and  $n_i$  (its eigenvariables) evolved towards equilibrium; and so on.

Figure 4.1 helps to visualise the change from the entropy potential (that is maximum at equilibrium) to the internal energy potential (that is minimum at equilibrium).

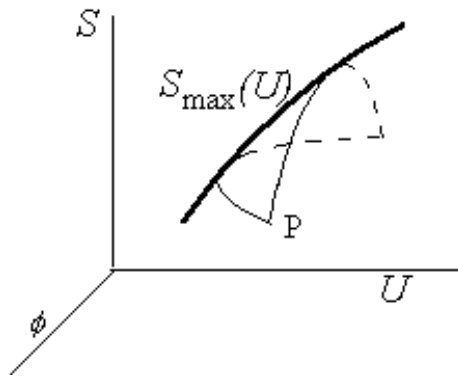


Fig. 4.1. Entropy variation with internal energy,  $U$ , and another unspecified non-equilibrium parameter,  $\phi$  (e.g. a gradient of temperature). Notice that from a non-equilibrium state P, the equilibrium state reached is different if the evolution is at  $U=\text{constant}$  (maximum entropy) or at  $S=\text{constant}$  (minimum energy).

From the Mathematics point-of-view, the different potentials are just Legendre transformations as used in other disciplines, as the change from the Lagrangian to the Hamiltonian function in Mechanics. In fact, the existence of potential functions is not genuine of Thermodynamics but a general rule in all branches of Physics, where one (the observer) tries to establish simple laws of Nature as: "this variable does not change with time" or "this variable takes a extremum value between two instants in time".

The interest in using these new thermodynamic functions lies in the following facts:

- Enthalpy,  $H$ , named by Kamerlingh Onnes in late 19th century as 'heat function', directly measures the heat exchanged by a closed system in an isobaric process (the most common case in all practical heat transfer cases), and directly measures heat-and-work exchange in flowing systems (the most important systems in engineering). The basic idea to keep in mind is that enthalpy-change,  $\Delta H$ , is the sum of energy-change,  $\Delta U$ , plus the work of expansion,  $\Delta(pV)$ .
- And  $A$  and  $G$  (traditionally named 'free energy' and 'free enthalpy', respectively), directly measure the exergy of a process at  $T$ -and- $V$  constant, and at  $T$ -and- $p$  constant, respectively, the latter of key interest for processes in the presence of an environment like the Earth atmosphere that can be assumed to keep constant  $T=T_0$  and  $p=p_0$ .

An isolated system evolves trying to maximise its entropy, at constant energy, but practical systems interact with their surroundings (perfect isolation is a limit idea), and tend to minimise the thermodynamic potential appropriate to their interaction with the environment. Thence:

- Isolated systems evolve such that  $dS/dt > 0$  (with  $dU/dt = 0$ ).
- Non-dissipative rigid systems evolve such that  $dU/dt < 0$  (with  $dS/dt = 0$ ).
- Real practical systems in an environment at constant  $T$  and  $p$  evolve such that  $dG/dt < 0$ .

This is, for instance, why a liquid system (e.g. water in a closed evacuated flask) reaches an equilibrium without all changing to a liquid state (that has less energy) or all changing to gas (that has more entropy); instead, a two-phase liquid-vapour equilibrium is established such that both effects balance:  $\Delta G_{\text{liq,vap}} = \Delta H_{\text{liq,vap}} - T\Delta S_{\text{liq,vap}} = 0$  (it will be shown as an [Exercise in Chapter 9](#) that this corresponds to  $T=373$  K for water at 100 kPa). Notice also a general rule that can be deduced from  $dG = dH - TdS < 0$ : as temperature increase, processes that increase entropy (mixing, gasification, decomposition, dissociation,

ionisation) are favoured against processes that decrease energy (that is also why water droplets and oxygen molecules do not separate from lighter nitrogen molecules in the air).

## EQUATIONS OF STATE AND THERMODYNAMIC COEFFICIENTS

Any of the thermodynamic potentials (e.g.  $G=G(T,p,n_i)$ ) holds all the thermodynamic information about a system at equilibrium. If we call equations of state (EOS) to its partial derivatives ( $\partial G/\partial T$ ,  $\partial G/\partial p$ ,  $\partial G/\partial n_i$ ), the set of all of them plus an irrelevant integration constant (because only increments of the potential function were defined) also hold all the information. We will also introduce some functions directly related to the second partial derivatives of the thermodynamic potentials, and call them thermodynamic coefficients because they do not change much with the state; similarly, the set of all thermodynamic coefficients plus two integration constants (one of them irrelevant) also holds all the information about a system at equilibrium. Taking Gibbs potential because its eigenvariables are the more natural, one gets from (4.4)

$$\partial G / \partial T \Big|_{p,n_i} = -S, \text{ and } S=S(T,p,n_i) \text{ is called energetic equation of state} \quad (4.5)$$

$$\partial G / \partial p \Big|_{T,n_i} = V, \text{ and } V=V(T,p,n_i) \text{ is called thermal equation of state} \quad (4.6)$$

$$\partial G / \partial n_i \Big|_{T,p} = \mu_i, \text{ and the } \mu_i=\mu_i(T,p,n_i) \text{ are called chemical equations of state} \quad (4.7)$$

But not all the equations of state are independent since they come from a single potential function and thus must verify that crossed second derivatives match, a mathematical property of analytical functions known as Schwarz relations in Mathematics and as Maxwell relations in Thermodynamics. That means e.g. that:

$$\frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T} \Rightarrow \frac{\partial(-S)}{\partial p} \Big|_{T,n_i} = \frac{\partial V}{\partial T} \Big|_{p,n_i} \quad (4.8)$$

and this is the reason why for systems of constant composition there is only need of one equation of state, chosen as the  $V=V(T,p)$  and simply named 'the equation of state' (but notice that it has not all the information; it remains  $\partial S/\partial T$ ).

From the second partial derivatives of the potentials we define the following so called thermodynamic coefficients:

- Specific (by unit of mass) or molar (by unit of amount of substance) isobaric thermal capacity:

$$c_p \equiv T \frac{\partial S}{\partial T} \Big|_{p,n_i} \quad (4.9)$$

- Isobaric thermal expansion (dilation):

$$\alpha \equiv \frac{1}{V} \frac{\partial V}{\partial T} \Big|_{p,n_i} \quad (4.10)$$

- Isothermal compressibility (similarly, an isentropic compressibility is also introduced):

$$\kappa \equiv \left. \frac{-1}{V} \frac{\partial V}{\partial p} \right|_{T, n_i} \quad (4.11)$$

### Exercise 1. Compatibility of equations of state

#### **SYSTEM STABILITY**

A system will evolve if some internal restraint is released (initial non-equilibrium) or if some constrain at the frontier is imposed (boundary non-equilibrium). We know that for an isolated system, an equilibrium state will be finally reached, although it might take longer than our life span (we call metastable equilibrium when the system appears to be stable for finite times under small enough disturbances). Stable systems return to their initial equilibrium state after a small perturbation is applied. Unstable systems move away from their initial equilibrium state to a distant equilibrium state after a small perturbation is applied, although metastable states may require a sizeable perturbation to become unstable. In Thermodynamics, when a system gets unstable (as when heating water a lot), a new phase appears (e.g. vapour), or new chemical compounds form, with different properties than the initial system (different densities, different compositions, etc.), i.e. a different equilibrium is reached.

Besides indicating when a system becomes unstable and phase transitions appear, the analysis of the stability teaches some general conditions for the thermodynamic functions. At a stable equilibrium,  $d^2S < 0$  implies that  $T > 0$ ,  $p > 0$  and  $\mu_i > 0$ , as well as  $c_p > 0$  (thermal stability),  $\kappa > 0$  (mechanical stability) and  $-\partial\mu_i/\partial n_j > 0$  (chemical stability). Notice that no restriction holds on dilation,  $\alpha$ , which, although usually positive, may be negative as in the case of pure water between 0 °C and 4 °C (there is some restriction, really, because from the generalised Mayer equation,  $c_p - c_v = \alpha^2 v T / \kappa$  (see below) and the stability conditions one may concludes that  $\alpha^2 < \kappa c_p / (v T)$ ). [A more extensive analysis of System stability can be found aside.](#)

From now on till the study of Mixtures (Chapter 7) we only consider constant-composition systems, i.e. evolutions that keep  $n_i = \text{constant}$ , what applies to pure chemical substances, and to closed mixtures without phase change, and, of course, without chemical reactions in any case.

#### **GENERAL DEPENDENCE OF STATE FUNCTIONS**

Many variables have been defined to characterise equilibrium states, and still some others are currently used, as the heat capacity at constant volume:

$$c_v \equiv T \left. \frac{\partial S}{\partial T} \right|_v \quad (4.12)$$

and the ratio of heat capacities:

$$\gamma \equiv \frac{c_p}{c_v} \quad (4.13)$$

also known as isentropic exponent because of its appearance in (1.13) (and sometimes also isentropic coefficient although it can be distinguished from a more general definition of the latter as  $k \equiv -\partial \ln p / \partial \ln v|_s$ , coinciding with the heat-capacity ratio in the ideal gas model).

Also a variable directly related to the isentropic compressibility can be defined that later will be shown to correspond to the speed of propagation of small perturbations (the speed of sound),  $c$ :

$$c \equiv \sqrt{\left. \frac{\partial p}{\partial \rho} \right|_s} = \sqrt{\frac{1}{\rho \kappa_s}} \quad (4.14)$$

Finally, a variable called compressibility factor (not to be confused with the compressibility coefficient) is introduced as:

$$Z \equiv \frac{pv}{RT} \quad (4.15)$$

where  $R$  is the gas constant. But as said before, there are only two intensive state variables independent, and all the others can be expressed as functions of these two. The natural choice for the two independent variables is  $T$  and  $p$ , and the general dependence of the others, based on the definition of the coefficients and on Maxwell relations) is as follows:

$$dv = \alpha v dT - \kappa v dp \quad (4.16)$$

$$\begin{aligned} ds &= \frac{c_p}{T} dT - \alpha v dp = \frac{c_p}{T} dT - \left. \frac{\partial v}{\partial T} \right|_p dp = \\ &= \frac{c_v}{T} dT + \frac{\alpha}{\kappa} dv = \frac{c_v \kappa}{\alpha T} dp + \frac{c_p}{\alpha T v} dv \end{aligned} \quad (4.17)$$

$$\begin{aligned} dh &= c_p dT + (1 - \alpha T) v dp = c_p dT + \left( v - T \left. \frac{\partial v}{\partial T} \right|_p \right) dp = \\ &= \left( c_v + \frac{\alpha v}{\kappa} \right) dT - \frac{1 - \alpha T}{\kappa} dv = \left( \frac{c_v \kappa}{\alpha} + v \right) dp + \frac{c_p}{\alpha v} dv \end{aligned} \quad (4.18)$$

$$\begin{aligned} du &= c_v dT + \left( \frac{\alpha T}{\kappa p} - 1 \right) p dv = c_v dT + \left( T \left. \frac{\partial p}{\partial T} \right|_v - p \right) dv = \\ &= (c_p - \alpha v p) dT - (\alpha T - \kappa p) v dp = \frac{c_v \kappa}{\alpha} dp - \left( \frac{c_p}{\alpha v} + p \right) dv \end{aligned} \quad (4.19)$$

$$dZ = Z \left( \alpha - \frac{1}{T} \right) dT - Z \left( \kappa - \frac{1}{p} \right) dp \quad (4.20)$$

after which the following relations can be obtained:

$$c_p = \left. \frac{\partial h}{\partial T} \right|_p \quad (4.21)$$

$$c_v = \left. \frac{\partial u}{\partial T} \right|_v \quad (4.22)$$

$$c_p - c_v = \frac{\alpha^2 v T}{\kappa} \quad (4.23)$$

$$\left. \frac{\partial c_p}{\partial p} \right|_T = -T \left. \frac{\partial^2 v}{\partial T^2} \right|_p = -v T \left( \alpha^2 + \left. \frac{\partial \alpha}{\partial T} \right|_p \right); \quad \left. \frac{\partial c_v}{\partial v} \right|_T = T \left. \frac{\partial^2 p}{\partial T^2} \right|_v \quad (4.24)$$

$$\left. \frac{\partial \kappa}{\partial T} \right|_p = - \left. \frac{\partial \alpha}{\partial p} \right|_T \quad (4.25)$$

$$\gamma \equiv \frac{c_p}{c_v} = \frac{\kappa}{\kappa_s} = \frac{c^2}{c_T^2} \quad (4.26)$$

where the isothermal speed of sound,  $c_T$ , is also shown for historical reasons (it is no longer used after experiments show that the actual speed of sound coincides with the isentropic model proposed by Laplace and not with the isothermal model proposed by Newton).

Notice that (4.24) gives the general dependence of  $c_p(p)$  and  $c_v(v)$  on the EOS  $f(p, v, T)=0$  ( $c_p(T)$  and  $c_v(T)$  are unrelated to the EOS). For instance, if the EOS is of the form  $v=Tf(p)$ , like for ideal gases,  $v=RT/p$ , then  $d^2v/dT^2|_p=0$  and  $c_p$  cannot depend on  $p$ , whereas if the EOS is of the form  $p=Tf(v)$ , like for ideal gases,  $p=RT/v$  (and for the van der Waal EOS too), then  $d^2p/dT^2|_v=0$  and  $c_v$  cannot depend on  $v$ . Another way to find the dependence of energy functions on non-thermal variables may be obtained from (4.18-22):  $dh=c_p dT+(v-T\partial v/\partial T|_p)dp$  and  $du=c_v dT+(T\partial p/\partial T|_v-p)dv$ .

Another variable of interest in isenthalpic expansions is the Joule-Kelvin coefficient, named for James Prescott Joule and William Thomson (later 1st Baron Kelvin) who established the effect in 1852 elaborating earlier work by Joule on gas expansion at constant internal energy). The Joule-Kelvin or Joule-Thomson coefficient,  $\mu_{JK}$  or  $\mu_{JT}$ , is defined as:

$$\mu_{JK} \equiv \left. \frac{\partial T}{\partial p} \right|_h = \frac{-(1-\alpha T)v}{c_p} = \frac{-1}{c_p} \left. \frac{\partial h}{\partial p} \right|_T \quad (4.27)$$

Usually, the Joule-Kelvin coefficient is positive and a gas cools a little when throttled (isenthalpic expansion), what may be used for refrigeration (e.g. at room temperature,  $\mu_{JK}=2.2 \cdot 10^{-6}$  K/Pa for air,  $\mu_{JK}=4.4 \cdot 10^{-6}$  K/Pa for CH<sub>4</sub>,  $\mu_{JK}=11 \cdot 10^{-6}$  K/Pa for CO<sub>2</sub>,  $\mu_{JK}=28 \cdot 10^{-6}$  K/Pa for NH<sub>3</sub>,  $\mu_{JK}=-0.34 \cdot 10^{-6}$  K/Pa for H<sub>2</sub>), but above a certain temperature, called inversion temperature (which depends on pressure) the coefficient becomes negative, and a decrease in pressure causes an increase in temperature. The J-K cooling may be important; e.g. if nitrogen from a bottle at 20 MPa and 300 K is let to flow along a thermally-insulated porous plug to 100 kPa, [the escaping gas is at 270 K](#) (below 0 °C). Be aware that the inversion temperature just mentioned relates to  $\partial T/\partial p|_h=0$ , which is unrelated to the temperature inversion defined in meteorology,  $dT/dz=0$  (i.e. the condition in which the temperature of the atmosphere increases with altitude instead of the normal decreasing).

Besides the above state variables, density ( $\rho=1/v$ ), exergy (that is a combination of system and environment variables as in (3.6)), mechanical energy (that is independent of the internal equilibrium state), total energy (that is the sum of internal energy and mechanical energy), some other mechanical variables (as the velocity or the height of the system), and a few physicochemical state variables to be Thermodynamic potentials and properties

introduced later, Thermodynamics makes use of a few path integrals (not state functions): work, heat, entropy generation and irreversibility. And the omnipresent universal gas constant  $R_u=8.314 \text{ J}/(\text{mol}\cdot\text{K})$ , that enters because of the arbitrary choice of Avogadro number (the number of entities taken as unit of amount of substance). Notice, by the way, that as no distinction is made on the writing of intensive variables (e.g.  $v$  is used for both specific volume and molar volume), so no distinction is made on the writing between the universal gas constant (the molar value given above) and the gas constant for a given substance,  $R=R_u/M$ , where  $M$  is the molar mass of the substance.

[Exercise 2. Generalised Mayer relation](#)

[Exercise 3. Sound speed in air and water](#)

## THE MATERIAL DATA NEEDED BY THERMODYNAMICS

### THERMODYNAMIC MODELS OF SUBSTANCES

We concentrate here on models for pure substances, leaving to Chapter 7: Mixtures, the modelling of mixtures (in terms of pure substance models).

It was said at the beginning of the Chapter that any potential function holds all the material properties of a system at equilibrium, but it is unusual to find the thermodynamic data in such a form, except for the most accurate reference data, nowadays compiled as a multiparameter empirical fitting of Helmholtz potential  $A(T,\rho)$ . Most usually, the data are presented in two functions  $\rho(T,p)$  and  $c_p(T,p_0)$ , or in non-dimensional form as  $Z(T,p)$  and  $c_p(T,p_0)/R$ , and always for a restricted region of validity in the  $T$ - $p$  field. For the condensed states of a substance  $p_0=100 \text{ kPa}$  is usually taken, but for the gaseous states (and condensed states based on it), it is preferred to base the data on  $p_0\rightarrow 0$  since in this limit  $\rho=p/(RT)$  and  $\partial c_p/\partial p=0$ .

Before stating any particular model, an important idea to keep in mind is that "there isn't any model covering all real details", a truth not only for thermodynamic data, but for any human-conceivable model. Empirical models can be very accurate on the small domain covered by the experimental data used to fit the parameters in the model, but they are usually nonsense when extrapolated. Theoretical models, based on molecular models and statistical mechanics, may be not so accurate, but they have fewer substance-dependent parameters, these parameters have physical meaning, and extrapolation may be good enough. Sometimes, however, this dichotomy is arbitrary, since there are semi-empirical equations, which combine features of theoretical and empirical equations (e.g. Antoine's equation versus Clausius-Clapeyron vapour-pressure equation, Redlich-Kwong versus van der Waals equation of state, or the virial expansion).

It is also customary to present the material data in a graphical form because the human brain works very well with graphics (but computers deal much better crunching numbers than recognising graphical patterns). The two functions,  $\rho(T,p)$  and  $c_p(T,p_0)$ , can be studied separately because their modelling is different, but we have preferred here to deal with complete models at once.

Brief, thermodynamic computations today are done manually when using simple models, or automatically for more accurate predictions using long lists of coefficients and some kind of polynomial or other type of function fitting of experimental data, and graphics may be used to plan or check computations.



Amongst the most simple data models, we have the following ones (the recommendation is, as for any model, to use the simplest model producing acceptable results):

### Perfect liquid model

The perfect liquid model, PLM (perfect here means  $c_p(T, p_0) = c = \text{constant}$ ), is also applicable to solids, and is:

$$\text{PLM: } \rho(T, p) = \rho = \text{constant, and } c_p(T, p_0) = c = \text{constant} \quad (4.28)$$

[A table of liquids and solids with their  \$\rho\$  and  \$c\$  values is presented aside.](#) No subindex is given to the thermal capacity here because with this model  $c_p$  and  $c_v$  coincide (and  $\alpha = 0$  and  $\kappa = 0$ ); this approximation may be judged by the case of water at 25 °C and 100 kPa:  $c_p = 4185 \text{ J/(kg}\cdot\text{K)}$  and  $c_v = 4140 \text{ J/(kg}\cdot\text{K)}$ , just 1%.

### Incompressible liquid model

The incompressible liquid model, ILM (not much used; incompressible here means  $\rho = \text{constant}$ ; it also applies to solids), is:

$$\text{ILM: } \rho(T, p) = \rho = \text{constant, and any } c_p(T, p_0), \text{ usually } c(T, p_0) = \sum a_i T^i \text{ with } a_i \text{ constant} \quad (4.29)$$

As an example, for liquid water at 100 kPa,  $c$  is nearly  $4220 \text{ J/(kg}\cdot\text{K)}$  at both 0 °C and 100 °C, with a minimum of  $4180 \text{ J/(kg}\cdot\text{K)}$  at around 35 °C. For liquid water at its vapour pressure,  $c = 4500 \text{ J/(kg}\cdot\text{K)}$  at 200 °C,  $5600 \text{ J/(kg}\cdot\text{K)}$  at 300 °C, growing to infinity at the critical point (374 °C). Notice that it may be inconsistent to account for  $T$ -changes on thermal capacity and not on density.

### Dilatable liquid model

The dilatable liquid model, DLM (used in dilatometric and thermoelastic problems), also applicable to solids, is:

$$\text{DLM: } \rho(T, p) = \rho_0 [1 - \alpha (T - T_0)], \text{ with } \rho_0 \text{ and } \alpha \text{ constant, and any } c_p(T, p_0) \quad (4.30)$$

[A list of thermal expansion coefficients is presented aside.](#) Notice that linear expansion coefficients,  $\alpha_{\text{lin}} = (1/L) \partial L / \partial T|_p = \alpha_{\text{vol}} / 3$ , are commonly tabulated and used in connection with solid materials (because only their main dimension is of interest), whereas volumetric expansion coefficients (4.10) are always used for fluids. In spite of the fact that for Materials Engineering the basic thermal data are thermal expansion and thermal conductivity, only trivial problems of dilatometry are usually tackled in Thermodynamics, leaving real thermoelastic problems (including thermal shock and thermal crack) to be analysed in Elasticity and Materials Science. When designing structures, mechanisms, and even coatings, it is important to account for expansion joints (if not, they will be established by themselves!). Notice, for instance, that reinforced concrete works well because steel-rods and concrete have similar expansion coefficients,  $\alpha = 12 \cdot 10^{-6} \text{ K}^{-1}$ ; otherwise tensions and cracks would develop when the temperature changed. Notice also that expansion may be due to other than thermal phenomena, as to moisture (e.g. moist wood expands, but moist ropes contract).

As an example, consider what might happen if a steel reservoir were totally filled with gasoline at a certain temperature (e.g. 20 °C), after some heating or cooling (e.g. by 10 °C). The thermal expansion of steel is  $\alpha_{\text{linear}}=12\cdot 10^{-6}$  1/K whereas for gasoline it is about  $\alpha_{\text{vol}}=900\cdot 10^{-6}$  1/K, what shows that, as in most cases, liquid reservoirs can be considered rigid relative to the thermal expansion of the liquid.

On heating, two problems may arise, depending on if the reservoir is open or closed. If open, the expanding liquid would overflow in the amount  $\Delta V=V\alpha\Delta T$ , where  $V$  is the volume of the reservoir, with a risk of an open fire. If closed, a pressure rise of  $\Delta p=V\alpha\Delta T / \kappa$  would result, probably breaking the reservoir.

On cooling, two problems may arise, depending on if the reservoir is open or closed. If open, the contracting liquid would ingest an amount of ambient air  $\Delta V=V\alpha\Delta T$ , with a risk of an internal explosion in the event of a spark. If closed, the contracting liquid would produce a void up to the vapour pressure of the liquid; in spite of the high vapour pressure of gasolines (they are mixtures with composition varied from winter to summer) would surely collapse the a thin-wall reservoir.

#### [Exercise 4. Effect of thermal expansion on a pendulum](#)

##### **Perfect gas model**

The perfect gas model, PGM, is the model most used in Thermodynamics. Perfect here means  $c_p(T,p_0)=c_p=\text{constant}$ , besides being an ideal gas. This model is:

$$\text{PGM: } \rho(T, p) = \frac{p}{RT}, \text{ (or more usually } pv=RT), \text{ and } c_p(T,p_0)=c_p=\text{constant} \quad (4.31)$$

[A data table of gases is presented aside](#), giving their molar mass  $M$  to compute  $R=R_u/M$ , their thermal capacity  $c_p$ , and some other properties.

##### **Ideal gas model**

The ideal gas model, IGM, usually refers just to the equation of state, but we said we only consider full models (equation of state and thermal capacity). This model can be based on the dynamics of point-like particles non-interacting among themselves, except for collisions. Notice that here 'ideal' means  $\rho=p/(RT)$ , or in the more usual form  $pv=RT$ , whereas in Fluid Mechanics 'ideal' usually means inviscid. The complete model is:

$$\text{IGM: } \rho(T, p) = \frac{p}{RT}, \text{ and any } c_p(T,p_0), \text{ usually } c_p(T,p_0)=\sum a_i T^i \text{ with } a_i \text{ constant} \quad (4.32)$$

A table of gases with their molar thermal capacity as a function of  $T$ , for very small pressures,  $p \rightarrow 0$ , is presented separately under [Thermal data](#). Notice that, although  $c_p(T,p \rightarrow 0)$  is monotonically increasing, a minimum appears at finite pressure values and low temperature; e.g. for dry air at 100 kPa,  $c_p=1040$  J/(kg·K) at 100 K,  $c_p=1007$  J/(kg·K) at 300 K, and  $c_p=1141$  J/(kg·K) at 1000 K.

##### **Van der Waals model**

The van der Waals model, VWM, is:

$$\text{VWM: } \left( p + \frac{a}{v^2} \right) (v - b) = RT, \text{ with } a \text{ and } b \text{ constant, and any } c_p(T, p_0) \text{ function (4.33)}$$

This model is the simplest one that can be used for the whole fluid range (gas and liquid regions), although it is more of academic interest than for real computations (its accuracy is not good). For this and most other models, no simple explicit expression for the density exists; this is a cubic equation of state in  $v$  (there have been many other cubic equation of state proposed, as Redlich-Kwong's, below). Other forms of (4.33) are  $Z = v/(v-b) - a/(vRT)$  and  $v^3 - (b + RT/p)v^2 + (a/p)v - ab/p = 0$ .

Van der Waals proposed that equation of state in 1875 trying to enhance the ideal gas model,  $pV = mRT$ , to incorporate two effects: the finite volume of the particles, and their attractive force. For the former effect, he proposed to replace the whole volume of the reservoir by the free volume available to the particles, once their own volume subtracted, i.e. passing from  $pV = mRT$  to  $p(V - N\pi d^3/6) = mRT$ , with  $N$  being the number of particles and  $d$  their diameter, assuming rigid spheres; notice that by experimentally measuring  $b$  for a substance, with (4.33), one can work-out the size of the molecules by  $b = N_A \pi d^3/6$ ,  $N_A = N/n$  being Avogadro's number). As for the second effect, he proposed to replace the actual pressure,  $p$ , in  $pV = RT$ , by the ideal pressure the particles would impose on the walls (which would be higher in absence of their mutual attraction),  $p + p_{\text{attr}}$ , with  $p_{\text{attr}}$  being proportional to the density of particles, squared to account for the surface effect (i.e. a spherical shell of particles pulling from a central particle,  $p_{\text{attr}} \propto 1/v^2$ , what finally yields (4.33). Notice that by experimentally measuring  $a$  for a substance, with (4.33), one can work-out the characteristic energy of interaction,  $\epsilon_0$ , for the important Lennard-Jones potential:  $u = 4\epsilon_0[(r_0/r)^{12} - (r_0/r)^6]$ , with  $r_0 = d/2$  being the molecular radius,  $r$  the intermolecular distance, and  $u$  the interaction energy between two molecules.

### Van der Waals reduced model

The van-der-Waals reduced model, VWRM, is the simplest universal analytical model, i.e. a model independent from the substance, whose properties only enter as scaling factors. This is a two-parameter equation of state, obtained by analytically solving for the constants  $a$  and  $b$  in (4.33) in terms of the  $p$ - $T$  values of the substance at its critical point ( $T_{\text{CR}}$  and  $p_{\text{CR}}$ , to be explained below), to yield ([see Problem 5](#)):

$$\text{VWRM: } \left( p_R + \frac{3}{v_R^2} \right) \left( v_R - \frac{1}{3} \right) = \frac{8}{3} T_R, \text{ and any } c_p(T, p_0) \text{ function (4.34)}$$

Any other bi-parametric equations of state could be used in reduced variables in a similar way, as for instance Redlich-Kwong's, but the numeric results would be different to the 3 and 8/3 in (4.34). In any case, all these reduced analytical universal models are inaccurate and only of academic interest.

### [Exercise 5. Van der Waals equation in reduced form](#)

### Redlich-Kwong model

The Redlich-Kwong model, RKM, proposed in 1949, is reputed to be one of the most accurate among all two-constant equations of state, also called van-der-Waals' derived equations (VWM extensions); nevertheless, deviations of saturated liquid molar volume for a wide variety of substances lay typical within  $(-20 \pm 20)\%$  of experimental values (for the whole temperature range). This model is a VWM

Thermodynamic potentials and properties

correction to the attractive term in (4.33),  $a/v^2$ , and, as most attraction-term extensions, is cubic in  $v$ . (extensions to the repulsive-term in (4.33),  $v-b$ , yield non-cubic equations). The Redlich-Kwong model is:

$$\text{RKM: } \left( p + \frac{a}{v(v+b)\sqrt{T}} \right) (v-b) = RT, \text{ with } a \text{ and } b \text{ constant, and any } c_p(T, p_0) \text{ function (4.35)}$$

### Virial expansion model

The virial expansion model, VEM (from Lat. *vis*, force), proposed by Kamerlingh-Onnes in 1912, gives an asymptotic series expansion to the thermal equation of state; i.e., we know that in the limit of very low pressure (above absolute zero temperature) all substances become ideal gases,  $p v = RT$  (or  $Z=1$ ), so it is natural to expect that the real behaviour can be approached by an expansion on pressure (or in the inverse of molar volume):

$$\text{VEM: } \begin{cases} \text{either } Z = 1 + Bp + Cp^2 + \dots \\ \text{or } Z = 1 + \frac{B'}{v} + \frac{C'}{v^2} + \dots \end{cases}, \text{ with } B=B(T), C=C(T)\dots, \text{ and any } c_p(T, p_0) \text{ function (4.36)}$$

The simplest virial equation only retains the second term ( $B(T)$  or  $B'(T)$ ,  $B'(T) \neq B(T)$ ), what yields a quadratic equation in  $v$  (not a cubic one, as for VWM, RKM and many others). It happens that the second virial coefficient is negative for low temperatures and positive for high temperatures, showing the dominance of intermolecular attraction over repulsion at low temperatures, and vice versa; e.g. when van der Waals equation is expanded in  $v$ , one gets  $Z = 1 + (b-a/(RT))/v + b^2/v^2 + \dots$

### Corresponding states model (introduction)

The molar volume of a fluid,  $v$ , at a given state,  $T$ - $p$ , depends a lot on the particular fluid at hand, but it is found in practice that if all values are scaled with values at the critical point of that substance, results are quite similar, i.e.  $v/v_{CR} = f(T/T_{CR}, p/p_{CR})$  is only slightly dependent on the substance, what may be used as an approximate prediction of  $p$ - $v$ - $T$  values based solely on critical point properties, and, of course, the particular equation of state used (the function  $f$ ). Any equation of state could be used to build such a universal  $p$ - $v$ - $T$  plot of 'corresponding states', as the VWRM presented above, but the most widely used corresponding states model, CSM, and the only one deserving that name here, is to be a graphical plot drawn by graphically fitting experimental data from several substances on a [Z-p<sub>R</sub> diagram](#). Because of the practical difficulty to differentiate and integrate graphically, auxiliary graphics are presented to help compute enthalpy and entropy changes, as explained in the analysis below.

The CSM is universal except for the scaling in terms of  $T_{CR}$  and  $p_{CR}$  (i.e., applicable to any substance without requiring special data about it, other than  $T_{CR}$  and  $p_{CR}$ ), it is simple (not requiring heavy computations but a look-and-see graph) and the most accurate of the models just presented (typical uncertainty around 5% except near the critical point), justifying a detailed description here, after the properties of a pure substance are first presented.

The corresponding states model can also be applied to the liquid state, but the uncertainty can be large. Some useful correlations for reduced liquid densities,  $\rho_R = \rho/\rho_{cr}$ , at saturation, are  $\rho_R = 1/Z_{cr}^{(1-T_R)^{2/7}}$ , and Thermodynamic potentials and properties

$\rho_R = 1 + (3/4)(1 - T_R) + (7/4)(1 - T_R)^{1/3}$ , the latter due to Guggenheim (1940s), who also proposed  $\rho_{R,v} = 1 + (3/4)(1 - T_R) - (7/4)(1 - T_R)^{1/3}$  for the reduced vapour density at saturation (for  $T_R > 0.5$ ).

A key point in evaluating the goodness of a thermodynamic model for a fluid is its ability to yield accurate vapour pressure data, what is best understood by using phase-change diagrams shown below.

## PROPERTIES OF A PURE SUBSTANCE AND THEIR GRAPHICAL PRESENTATION. DIAGRAMS

### Simple pure substances

Thermodynamic problems usually focus on simple chemically-pure substances and their mixtures, mostly fluids: water, air, alcohols, short-chain hydrocarbons, and the like. A substance is a chemically identified pure or mixed matter (solid or fluid): water, wine, oil, blood, DNA. A large share of substances of practical interest are molecules composed of just hydrogen, H, and C, N, O and F atoms (see the [periodic table](#)); including the lower row, Si, P, S and Cl one covers practically all fluids of interest.

Substances with small molecules show well-defined phase-transition points (e.g. 273 K and 373 K for solid-liquid and liquid-gas transitions of pure water at 100 kPa without kinetic effects), whereas substances with large molecules (macromolecules usually refers to  $M \gg 1$  kg/mol, i.e. with more than 100 atoms per molecule) do not show so sharp phase-transition points, and are only stable in condensed form because they chemically decompose on heating, before boiling.

Materials are solid bodies with intrinsic properties (apart of the shape) that render them useful, mainly for structures, but also for electronics, optics, biomedicine, etc. They are usually classified in terms of physical behaviour as: ceramics, metals, polymers and composites; although other times they are classified in terms of their application (structural materials, electronic materials, and so on).

Except for air and water that are ubiquitous, most other working substances are procured from a local supplier, what may be a nuisance for 'special-container substances' like gases ([there are some additional notes on natural and commercial gases aside](#)).

Of course, the 'pure substance' is just an idealisation: there are always impurities in any real substance, but a 90%-pure substance (10% impurities) may be good enough for some purposes, a 99%-pure substance is usually named 'commercially pure', and a 99.99%-pure is usually referred as 'laboratory pure', although it depends a lot on the application (e.g. in the electronics industry, sometimes 6 nines are required, i.e. 99.9999% purity, less than 1 ppm of impurities). Besides, if there is no segregation within a mixture during a thermodynamic process, the mixture may be treated as a pure substance, as usually made with air (until segregation of one of its components, water vapour, is studied in the Humid Air chapter).

Properties of matter (as a system of  $N$  elementary particles of type say  $a$ ) may be of three general types: constitutive, if only depend on  $a$ ; colligative, if only depend on  $N$ ; and additives, if they depend on the product of  $N$  and an attribute of  $a$  (e.g. mass, momentum, energy, entropy).

Simple chemically-pure substances, like water, usually have simple molecules, i.e. of a few atoms, and their thermal behaviour is as follows (think on a cylinder-piston system to avoid contact with ambient

air). At low enough temperatures (near  $T=0$  K) they are all crystalline solids (except the rarity of quantum helium). When the solid is heated enough, it always melts at a precise temperature known as melting temperature,  $T_m$  (or freezing temperature,  $T_f$ ), which depends very little on pressure. When the liquid is heated enough, it boils at a precise temperature known as boiling (or condensing) temperature,  $T_b$ . When the gas is heated enough, it decomposes in atoms and ions and Chemical Thermodynamics is needed to analyse these reactions. These solid-liquid-gas phase transitions apply only to few-atom molecular substances and crystalline networks (metallic and ceramic), and only for quasi-static processes, but do not apply to many-atom molecular substances like ceramic or plastic macromolecules that yield amorphous solid phases, and do not show well-defined melting temperatures but glass-transition temperatures, where thermal expansion has a jump (in crystalline solids it is density that shows a jump).

### Phase diagrams for a pure substance

Phase transformations can be represented in a  $p$ - $T$  diagram (called phase diagram for a pure substance), as shown in Fig. 4.2 for the case of pure water at equilibrium (in a metastable state, distilled water at 100 kPa may be kept as undercooled liquid well below 0 °C, and as superheated liquid above 100 °C). Although water is perhaps the simple substance showing more complex behaviour, all simple-fluids have nearly the same layout, particularly if only the region close to the liquid-vapour equilibrium is of interest, with a critical point CR, a triple point TR and the normal boiling point BP in between.

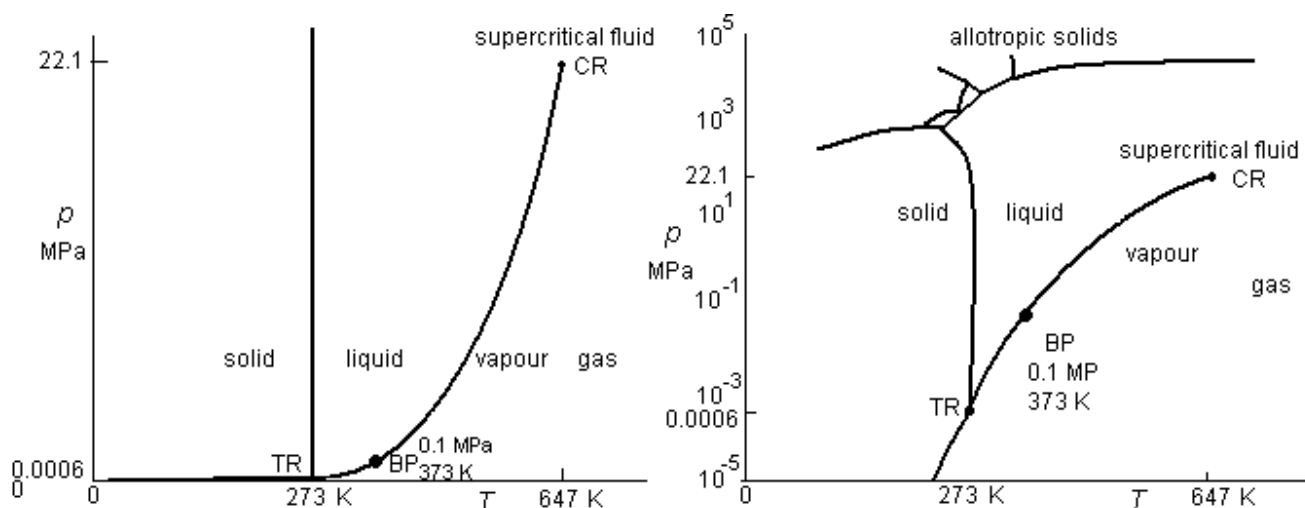


Fig. 4.2. Phase diagram for  $H_2O$  to scale. Notice how different they may look in linear scale, and in logarithmic scale for pressure.

A first feature of  $p$ - $T$  diagrams is a quasi-vertical line separating the solid and liquid phases, showing the fact that the melting point scarcely depends on pressure (except at huge pressures, of interest only in geology and astrophysics, up to now, where all substances tend to the solid state, usually a different allotrope of the normal solid, see Fig. 4.2b). Although the melting line is practically vertical in all cases, its inclination is usually exaggerated in sketches to show that most substances have a positive slope, but water and a few rare others have negative slopes, as [later explained](#).

A second feature is that the boiling temperature depends a lot on applied pressure and two limits appear in the vapour pressure curve, known as triple point (TR) and critical point (CR) respectively (Fig. 4.2). For low enough pressures, the solid directly sublimates to gas without passing through the liquid phase, and for high enough pressures the liquid does not boil but expands and expands without phase change.

Because a smooth process (without phase changes) can join a liquid state to a gas state, and vice versa, around the critical point, it is a matter of consensus to distinguish between a liquid state and a gas state; usually, a fluid state is named 'liquid' if it is below its critical pressure and to the left of the vapour-pressure curve in Fig. 4.2; a fluid state is named 'vapour' if it is below its vapour-pressure curve and to the left of its critical temperature; a fluid state is named 'gas' if it is below its critical pressure and to the right of its critical temperature; finally, a fluid state is named 'supercritical fluid' if it is above its critical pressure (usually in the range  $p/p_{CR}=1..2$  and  $T/T_{CR}=1.0..1.1$ ). The term 'vapour pressure curve' usually refers to the liquid-vapour-equilibrium (LVE) vapour pressure, but sometimes the solid-vapour-equilibrium curve is included.

The liquid state is not abundant in the universe, with the remarkable exception of water on Earth, but there can be realised very-low-temperature liquids (cryogenic fluids, with quantum helium being the only substance remaining liquid as  $T \rightarrow 0$  for  $p < 2.5$  MPa), and very-high-temperature liquids (liquid metals; at room pressure, hafnium is a liquid from 2500 K to 4900 K).

Notice that the melting line cannot end in a critical solid-liquid point but splits at additional triple points (solid-solid-liquid), because there cannot be a smooth transition from a crystalline symmetry to the liquid randomness. Triple points of pure substances of low molar mass are fixed points, i.e. can only occur at a precise temperature and pressure, and they are key points in [thermometry](#). The approximation of triple-point data by the melting temperature and its corresponding vapour pressure is usually good enough for most purposes (e.g. the triple point of water is  $T_{TR} \equiv 273.16$  K (by definition of the temperature unit) and  $p_{TR} \equiv 611 \pm 1$  Pa (by experimentation), whereas the melting point is 273.15 K and its corresponding vapour pressure using Antoine equation, to be explained in Chapter 6: Phase change, is  $p_v(273.15 \text{ K}) = 620$  Pa; a very good approximation.

A final feature is that the axes ( $T=0$ ,  $p=0$ ) in the phase diagram are unattainable limits (nowadays some  $10^{-6}$  K and some  $10^{-12}$  Pa have been reached, but 0 K would imply an infinite series of cooling steps and 0 Pa would imply lack of any mass at sight). As this singular point is approached, the the slope of the sublimation curve tends to zero in the  $p$ - $T$  diagram, and to infinity in a  $\ln p$ - $T$  diagram

### Other thermodynamic diagrams

Thermodynamic diagrams are graphical plots of, either the substance properties (e.g. [the  \$p\$ - \$h\$  diagram for water](#)), or some particular processes applied to the working substance (as used in most thermodynamic exercises, e.g. [Ex. 2.3](#)).

Besides the  $p$ - $T$  or phase diagram, several other diagrams are in current use to present pure-substance data or to sketch particular processes of a pure substance, as shown in Fig. 4.3. The  $p$ - $v$  diagram is mainly used to sketch mechanical processes like cylinder-piston evolutions. The  $p$ - $h$  diagram is most used to present data for substances, and in refrigeration problems. The  $T$ - $s$  diagram is the most used in teaching and sketches of general process. The  $h$ - $s$  diagram is the traditionally used in steam problems. Notice that the triple point in the  $p$ - $T$  diagram becomes a triple line in the other diagrams, due to the coexistence of three phases with different properties, whereas the critical point remains a point because the two coexisting phases have the same properties. It must be noticed also that, to present a complete set of data for a

substance, one needs one potential, or two equations of state, so that it is not enough to have the family of isochors (lines of constant volume) in a  $p$ - $T$  diagram, neither the family of isotherms in the  $p$ - $h$  diagram, nor the family of isobars in a  $T$ - $s$  diagram; but the family of isentropics in a  $p$ - $h$  diagram suffice, as well as the family of isobars in a  $h$ - $s$  diagram, because the potential  $h(s,p)$  is made available in both cases.

[Exercise 6. The  \$h\$ - \$s\$  or Mollier diagram](#)

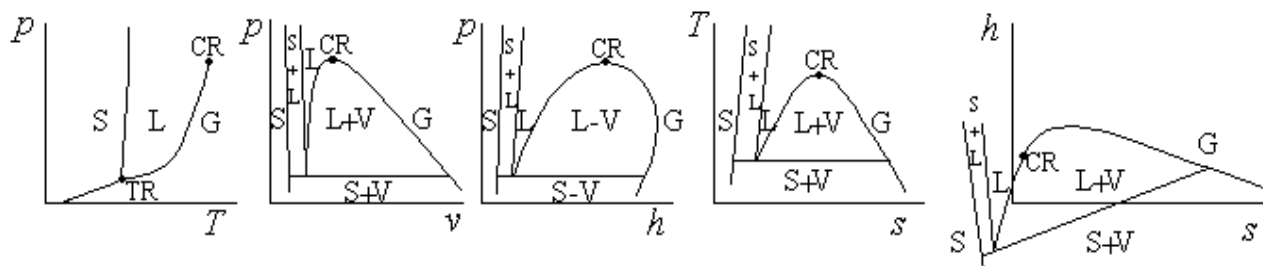


Fig. 4.3. Main thermodynamic diagrams used to plot pure-substance data or to sketch particular processes.

More accurate than the graphical presentation of data (although less handy) is a set of tables with numerical values, usually a double entry table for the gas phase and a single entry one for the saturated states.

Notice that some facts on the behaviour of pure substances may be misleading when mixtures are considered. Some examples follow: One may believe that water cannot be solid or gas at room conditions; one says “at 15 °C and 100 kPa, water is a liquid” when one should say “at 15 °C and 100 kPa, pure water is a liquid”, but at the same conditions water is a gas when dissolved in air. One may believe that air cannot be in the liquid state at room conditions, in spite that all fish and aquatic plants breathe it (gases and solids dissolved in liquids are in the liquid state). One may believe that the critical point marks the maximum temperature for a liquid, without realising that the critical point for mixtures departs a lot from the critical points of pure substances. One may believe that the maximum density for a substance is when as a pure solid (or pure liquid in some exceptional cases like water or silicon), without ever thinking on the possibility that a mixture with another substance might enclose more molecules per unit volume than the pure condensed phase (e.g. one litre of metal hydride may hold more hydrogen than if filled with liquid hydrogen).

**Corresponding states model (analysis)**

As said before, graphical representations of simple pure-substance data, on the same diagram, have all the same topology (the one shown in Fig. 4.3), suggesting that if conveniently scaled with the triple, or better the critical point data (because this is the key point in the whole fluid phase, liquid and vapour), they might match. Of course real substances do not match perfectly when plotted in reduced variables, but the accuracy may be acceptable and the study worth enough (it would perfectly match if the molecular model had only two parameters, as in the Lennard-Jones model referred above, or for any other two-parameters model as VWM or RKM).

The most widely used corresponding states diagram (see above how they can be generated) comes back to Hougen and Watson in 1900, who chose an overlay fitting with  $Z_{CR}=0.27$  (see following point), and is sketched in Fig. 4.4 and plotted aside under [Thermal data](#):



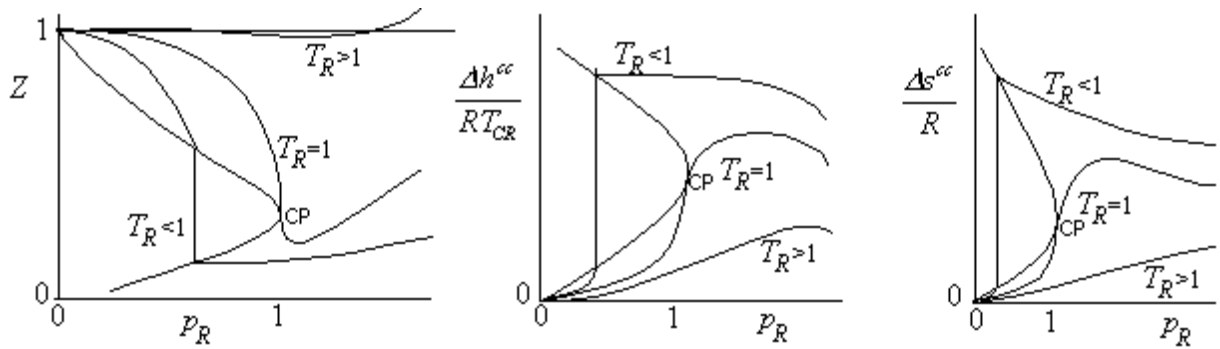


Fig. 4.4. Sketch of the compressibility factor,  $Z$ , and the compressibility corrections  $\Delta h^{cc}$  and  $\Delta s^{cc}$ , in terms of reduced pressure and temperature,  $T_R \equiv T/T_{CR}$  and  $p_R \equiv p/p_{CR}$ , for the corresponding states model (CSM).

The value of the compressibility factor at the critical point,  $Z_{CR} = p_{CR}v_{CR}/(RT_{CR})$  (not to be confused with the compressibility coefficient,  $\kappa$ , which tends to infinity at the critical point), most clearly shows the difference between reduced models and experiments. Experimental data show that  $Z_{CR}(\text{H}_2\text{O})=0.23$ ,  $Z_{CR}(\text{NH}_3, \text{ alcohols, ketones...})=0.24..0.26$ ,  $Z_{CR}(\text{hydrocarbons})=0.26..0.28$ , and  $Z_{CR}(\text{permanent gases})=0.28..0.30$ , whereas for the analytical models  $Z_{CR}(\text{PGM, IGM})=1$ ,  $Z_{CR}(\text{vWRM})=0.38$ ,  $Z_{CR}(\text{RKRM})=0.32$ , and the choice of  $Z_{CR}(\text{CSM})=0.27$ . Instead of  $Z_{CR}$ , other reduced parameters may be chosen to compare models with experiments; e.g. the reduced boiling temperature,  $T_{bR} \equiv T_b/T_{CR}$ , the reduced Boyle's temperature,  $T_{BR} \equiv T_B/T_{CR}$  (see following point), the reduced inversion temperature,  $T_{IR} \equiv T_i/T_{CR}$ , the acentric factor (see following point), or the complete vapour-pressure curve (in reduced variables); a simple approximation to the latter is Guggenheim's rule,  $\ln p_R = A(1 - 1/T_R)$ , with  $A \approx 6$ , as explained in [Chapter 6: Phase change](#). For many substances, the reduced boiling-point temperature is  $T_{bR} = 0.6$  (e.g. 0.58 for  $\text{H}_2\text{O}$ , 0.59 for  $\text{NH}_3$ , 0.64 for  $\text{C}_4\text{H}_{10}$ , 0.71 for  $\text{CO}_2$ , 0.66 for  $\text{CH}_3\text{OH}$ , 0.61 for  $\text{N}_2$ , 0.62 for  $\text{C}_3\text{H}_8$ ). The reduced triple-point temperature, however, has large scatter:  $T_{TPR} = 0.42$  for  $\text{H}_2\text{O}$  ( $p_{TPR} = 0.0045$ ),  $T_{TPR} = 0.71$  for  $\text{CO}_2$  ( $p_{TPR} = 0.014$ ),  $T_{TPR} = 0.48$  for  $\text{NH}_3$  ( $p_{TPR} = 0.0088$ ),  $T_{TPR} = 0.23$  for  $\text{C}_3\text{H}_8$  ( $p_{TPR} = 0.023$ ), etc. If critical-point data for a substance is not available, a crude approximation in terms of the normal boiling point is:  $T_{CR} \approx 1.6T_b$ ,  $\rho_{CR} \approx 0.37\rho_b$ , and  $p_{CR} = Z_{CR}\rho_{CR}RT_{CR}$ .

Enthalpy and entropy corrections to the ideal gas state are performed with the help of the auxiliary graphs [h-p<sub>R</sub>](#) and [s-p<sub>R</sub>](#). Other functions are computed from enthalpy and entropy; e.g.  $\Delta u = \Delta h - \Delta(pv)$ . The explanation of how the enthalpy and entropy correction can be computed from the compressibility factor is very illustrative of how to use the data available in any model (CSM, VWM, RKM...). To begin with, only increments of energy and entropy were defined operationally (Eqs. 1.3 and 2.6); thus the problem is how to compute  $\Delta h$  and  $\Delta s$  from the given data  $v(T, p)$  and  $c_p(T, p \rightarrow 0)$ . The general expressions to do that are (4.17) and (4.18), and the integration can be performed along any desirable path since  $h$  and  $s$  are state functions and thus path-independent. On view of the available data, it is advantageous to follow the three-step path shown in Fig. 4.5 since this is the only one that only requires the values of  $c_p$  at very low pressure, thus (4.17) and (4.18) develop to:

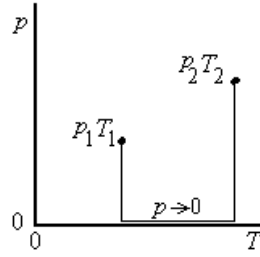


Fig. 4.5. This is the best integrating path from 1 to 2, on view of the data at  $p \rightarrow 0$ .

$$h_2 - h_1 = \int_{p_1}^{p \rightarrow 0} (1 - \alpha T_1) v dp + \int_{T_1}^{T_2} c_p(T, p \rightarrow 0) dT + \int_{p \rightarrow 0}^{p_2} (1 - \alpha T_2) v dp \quad (4.36)$$

$$s_2 - s_1 = \int_{p_1}^{p \rightarrow 0} (-\alpha v) dp + \int_{T_1}^{T_2} \frac{c_p(T, p \rightarrow 0)}{T} dT + \int_{p \rightarrow 0}^{p_2} (-\alpha v) dp \quad (4.37)$$

and in reduced variables, with  $v = ZRT/p$  from (4.15) and  $\alpha v = \partial v / \partial T|_p$  from 4.16):

$$\frac{h_2 - h_1}{RT_{CR}} = T_{R_1}^2 \int_{p_{R_1}}^{p_{R \rightarrow 0}} \left. \frac{\partial Z}{\partial T_R} \right|_{p_R} \frac{dp_R}{p_R} + \int_{T_1}^{T_2} \frac{c_p(T, p \rightarrow 0)}{R} dT_R + T_{R_2}^2 \int_{p_{R \rightarrow 0}}^{p_{R_2}} \left. \frac{\partial Z}{\partial T_R} \right|_{p_R} \frac{dp_R}{p_R} \quad (4.38)$$

$$\frac{s_2 - s_1}{R} = \int_{p_{R_1}}^{p_{R \rightarrow 0}} \left( Z + T_{R_1} \left. \frac{\partial Z}{\partial T_R} \right|_{p_R} \right) \frac{dp_R}{p_R} + \int_{T_1}^{T_2} \frac{c_p(T_R, p \rightarrow 0)}{RT_R} dT_R + \int_{p_{R \rightarrow 0}}^{p_{R_2}} \left( Z + T_{R_2} \left. \frac{\partial Z}{\partial T_R} \right|_{p_R} \right) \frac{dp_R}{p_R} \quad (4.39)$$

what may be viewed as an ideal gas contribution (that may be further approximated with the perfect gas model), plus some compressibility corrections in the way::

$$h_2 - h_1 = (h_2^{id} - h_1^{id}) - Dh_2^{cc} + Dh_1^{cc} \quad (4.40)$$

$$s_2 - s_1 = (s_2^{id} - s_1^{id}) - Ds_2^{cc} + Ds_1^{cc} \quad (4.41)$$

where:

$$\frac{\Delta h^{id}}{RT_{CR}} \equiv \int_{T_1}^{T_2} \frac{c_p(T_R, p \rightarrow 0)}{R} dT_R, \quad \frac{\Delta h^{cc}}{RT_{CR}} \equiv T_R^2 \int_{p_{R \rightarrow 0}}^{p_R} \left. \frac{\partial Z}{\partial T_R} \right|_{p_R} \frac{dp_R}{p_R} \quad (4.42)$$

$$\frac{\Delta s^{id}}{R} \equiv \int_{T_1}^{T_2} \frac{c_p(T_R, p \rightarrow 0)}{RT_R} dT_R - \ln \frac{p_{R_2}}{p_{R_1}}, \quad \frac{\Delta s^{cc}}{R} \equiv \int_{p_{R \rightarrow 0}}^{p_R} \left( Z - 1 + T_R \left. \frac{\partial Z}{\partial T_R} \right|_{p_R} \right) \frac{dp_R}{p_R} \quad (4.43)$$

### Boyle's temperature. Inversion temperature. Acentric factor

Boyle's temperature,  $T_B$ , is defined as the isotherm that goes out from  $p=0$  with zero slope in the  $Z$ - $p_R$  diagram, i.e. it is the temperature at which real gas behaviour departs the least from the ideal gas model as pressure increases (the closest to the horizontal line  $Z=1$  in the  $Z$ - $p_R$  diagram); some experimental values for Boyle temperature are:  $T_B(\text{N}_2)=327$  K ( $T_{BR}=T_B/T_{CR}=2.60$ ),  $T_B(\text{O}_2)=405$  K ( $T_{BR}=2.61$ ),  $T_B(\text{Ar})=410$  K ( $T_{BR}=2.72$ ),  $T_B(\text{CO}_2)=713$  K ( $T_{BR}=2.35$ ),  $T_B(\text{H}_2)=110$  K ( $T_{BR}=3.3$ ),  $T_B(\text{CH}_4)=510$  K ( $T_{BR}=2.67$ ), to be compared with  $T_{BR}(\text{VWRM})=27/8=3.4$ , and  $T_{BR}(\text{CSM})=2.5$ . The fact that normal temperature on Earth (around 300 K) is close to air Boyle's temperature (around 350 K) makes the ideal gas model applicable to air at relatively large pressure (which is not the case for most other gases).

The inversion temperature,  $T_I$ , is the temperature separating the region of heating from the region of cooling, when adiabatically throttling a gas, and corresponds to  $\mu_{JK}=0$  in (4.27); some experimental values for the inversion temperature are:  $T_I(\text{N}_2)=620$  K ( $T_{IR}=4.9$ ),  $T_I(\text{O}_2)=765$  K ( $T_{IR}=4.9$ ),  $T_I(\text{He})=45$  K ( $T_{IR}=8.5$ ),  $T_I(\text{Ne})=270$  K ( $T_{IR}=6.1$ ),  $T_I(\text{H}_2)=200$  K ( $T_{IR}=6.1$ ),  $T_I(\text{CO}_2)=1250$  K ( $T_{IR}=4.1$ ),  $T_I(\text{CH}_4)=1010$  K ( $T_{IR}=5.3$ ), to be compared with  $T_{IR}(\text{VWRM})=27/4=6.8$ , and  $T_{IR}(\text{CSM})\approx 5$ .

The acentric factor,  $\omega$ , introduced by [Pitzer](#) in 1955 as a measure of the non-sphericity of a gas molecule. He realised that monoatomic gases (really all noble gases except helium) at  $T_R=0.7$  (a reduced temperature he chose for comparisons), have a reduced vapour pressure,  $p_{vR}$ , close to  $p_{vR}=0.1$  (i.e.  $\log_{10} p_{vR}=-1$ ). Besides, he realised that other gases departing the same amount from that reference point, have similar departures in other reduced variables. He then proposed to define the acentric factor as  $\omega \equiv -1 - \log_{10} p_{vR}|_{T_R=0.7}$ , and use it as a third parameter in the enhanced corresponding state model described below. [Values of Pitzer's acentric factors can be found aside](#), where it can be seen that neon, argon and xenon have  $\omega \approx 0$ .

Furthermore, the acentric factor may be used to have a reduced vapour pressure curve, more accurate than Guggenheim's approximation, in the form  $\ln p_R = 5.4(1+\omega)(1-1/T_R)$ .

### Equations of state with three or more parameters

The corresponding states method developed above (CSM) gives all the volumetric information of a fluid,  $v(T,p)$ , in terms of only two parameters for each fluid,  $T_{CR}$  and  $p_{CR}$ . Several enhanced corresponding states methods have been developed, introducing additional parameters of the substance. The first choice might seem to be a three-parameter model based on  $T_{CR}$ ,  $p_{CR}$  and  $v_{CR}$  (or  $Z_{CR}=p_{CR}v_{CR}/(RT_{CR})$ , but the experimental measure of  $v_{CR}$  has a large uncertainty (the position of a maximum), and it is preferable to use the tern  $T_{CR}$ ,  $p_{CR}$  and  $\omega$  (the acentric factor, defined just above), basically because two sets of graphics (or tabulations) are enough, i.e.  $Z(p_R, T_R, \omega) = Z_0(p_R, T_R) + \omega Z_1(p_R, T_R)$  at least for  $|\omega| < 0.2$ , where  $Z_0(p_R, T_R)$  is a similar graph to the [Z\(p<sub>R</sub>, T<sub>R</sub>\)-graph](#) used in the simple corresponding state model (CSM), which was prepared to best fit hydrocarbon gases with  $Z_{CR}=0.27$ , but now fitting the noble-gas data (other than He, as said), which have  $Z_{CR}=0.29$  (and  $p_{vR}|_{T_R=0.7}=0.1$ , whereas in our [Z\(p<sub>R</sub>, T<sub>R</sub>\)-graph](#)  $p_{vR}|_{T_R=0.7} < 0.1$ ;  $p_{vR}|_{T_R=0.7} \approx 0.08$ ).

As a substitute of this three-parameters extended corresponding-states-method, one may use the following truncated virial expansion model in reduced variables, based on the tern  $T_{CR}$ ,  $p_{CR}$  and  $\omega$ , that we name acentric virial model, (AVM), and which gives accurate predictions for most real gases (except highly polar molecules like water) in the range  $0.6 < T_R < 2$ :

$$Z = 1 + Bp = 1 + \left[ \left( \frac{0.083}{T_R} - \frac{0.422}{T_R^{2.6}} \right) + \omega \left( \frac{0.139}{T_R} - \frac{0.172}{T_R^{5.2}} \right) \right] p_R, \text{ and any } c_p(T, p_0) \text{ function (4.44)}$$

[Exercise 7. Corresponding states corrections](#)

[Exercise 8. Corrections based on an analytical equation of state](#)

## **TYPE OF PROBLEMS**

The housekeeping problems of how thermodynamic variables are dependent on each other, constitutes the bulk of the problems in this Chapter that is the most formal and mathematical of all. The type of problems may be quite varied:

1. Deduce one particular equation from others (many, according to the many equations presented).
2. Find the redundancy in some thermodynamic data given.
3. Deduce the shape of different curve families in the different diagrams.
4. Extract indirect thermodynamic functions from usual diagrams.
5. Compare the accuracy (and burden) of different thermodynamic models.
6. Use the corresponding states model to quickly elucidate the goodness of more simple models.

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